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(54) SILVER HALIDE EMULSION AND SILVER HALIDE PHOTOGRAPHIC SENSITIVE MATERIAL**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a silver halide emulsion and a silver halide photographic sensitive material having high illumination, improved off-track and/or high sensitivity-reduced fog.

SOLUTION: This silver halide emulsion contains silver halide grains contg. a metallic compd. dopant and an iridium compd. dopant in combination. The metallic compd. dopant is a complex with at least one kind of metal among the groups 3-7 or 9-14 metals of the 4th, 5th and 6th periods of the Periodic Table as a center or its metallic ion. Parts contg. the iridium compd. dopant and parts contg. the metallic compd. dopant in the grains are different from one another.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the silver halide emulsion with which high illuminance non-** is characterized by being improved and high-sensitivity-ized in detail about silver halide photosensitive material.

[0002]

[Description of the Prior Art] It goes over the silver halide photosensitive material by which current marketing is carried out, and the image formation approach using it variously, and they are used for all fields.

[0003] Fogging is low, the shape of a grain is fine, asking in common for the application and the purpose, although it is various has [in high sensitivity] little change of sensibility and gradation by change of an exposure illuminance at high contrast, and the halogen presentation of the silver halide used into sensitive material is excelling in processability. In order to attain this purpose, the attempt which uses metallic compounds for a silver halide emulsion has been examined for many years.

[0004] Generally as a dopant generally used in silver halide photosensitive material, the 6 coordination metal complex of a regular-octahedron mold is known. A "dopant" points out all the compounds included in silver halide crystals in addition to silver or halide ion here. Especially as for the metal complex whose central metals are transition metals (three to 12 group of the element periodic table), much researches are made for the purpose of reforming of a silver halide emulsion as a dopant.

[0005] When the reciprocity law of a photograph is materialized, the sensibility of a photographic emulsion will become fixed regardless of exposure reinforcement and each value of the exposure time, if those products are the same values (namely, when there is no reciprocity law failure).

[0006] Although light exposure of high intensity reciprocity law failure is equivalent in this invention, when the exposure times differ, the sensibility of a photographic emulsion means [the exposure time] the phenomenon which becomes so low that it is short. Similarly, although light exposure of low intensity reciprocity law failure is equivalent, when the exposure times differ, the sensibility of a photographic emulsion means [the exposure time] the phenomenon which becomes so low that it is long.

[0007] At the time of particle nucleation, the metal introduced at the time of particle growth goes into a particle as a dopant, and it is said to the research disclosure 308118th and an I-D chapter that the photograph engine performance is changeable depending on the location in those content and a particle.

[0008] It is known for the case where a transition-metals compound is added during silver halide particle formation, and the case where it adds after precipitate of a silver halide particle that there is a difference remarkable in the photograph effectiveness of the transition-metals compound in a silver halide emulsion. Although in the case of the former a transition-metals compound is incorporated as a dopant in a silver halide particle and the amount is very few, generally changing the photograph engine performance effectively is known.

[0009] In the case of the latter, a transition-metals compound is adsorbed on a particle front face, but a

particle cannot often be approached by the interaction with a deflocculant in many cases. A transition-metals compound is added after particle formation, and in order to acquire the same effectiveness as the case where the transition-metals compound is incorporated inside the silver halide particle, it is necessary to add a more high-concentration transition-metals compound. That is, when a transition-metals compound is added in chemical sensitization, generally it is recognized that the photograph effectiveness is hard to be acquired, and the transition-metals compound has been used as a dopant during particle formation.

[0010] This research disclosure IIIA chapter has a publication about the transition-metals compound introduced into chemical sensitization again at the research disclosure 17643rd and IA chapter about the transition-metals compound introduced during precipitate of a particle about the difference in the technique of metal doping added to an emulsion during formation of a silver halide particle, and the metal sensitizer by adding a transition-metals compound to an emulsion after formation of a silver halide particle.

[0011] In U.S. Pat. No. 4,126,472, a silver halide emulsion is riped under existence of a 10^{-6} to ten - four mols [per one mol of silver halides] water-soluble iridium salt, and using iridium as a particle surface treatment agent is indicated.

[0012] Reduction of high illuminance non-** in the silver halide emulsion which becomes the Europe patent No. 242,190 from the silver halide particle generated under one or more sorts of complex compound existence among the trivalent rhodiums which have 3, 4, 5, or six cyanides ligands is indicated.

[0013] The approach including the process which makes a silver halide particle under existence of the deflocculant which becomes U.S. Pat. No. 3,690,888 mainly from an acrylic polymer in the process of the silver halide containing polyvalent metal ion is indicated. As polyvalent metal ion, a bismuth, iridium, lead, and/or osmium ion are mentioned especially.

[0014] on the other hand -- U.S. Pat. No. 4,835,093 -- said -- No. 4,933,272 -- said -- No. 4,981,781 -- said -- No. 5,037,732 -- said -- No. 4,937,180 -- said -- the ligand which can form a metal ion and a coordinated complex in No. 4,945,035 -- the particle crystal structure -- it can enter -- transition-metals ion -- amelioration of the photograph engine performance which is not realized depending on independent inclusion is indicated.

[0015] It is prepared by the Europe patent No. 336,425, said 336,426 numbers, JP,2-20853,A, and 2-20854 under existence of the rhenium of 6 coordination which has at least four cyanogen ligands, a ruthenium, an osmium, and an iridium metal complex, and the silver halide emulsion aiming at the improvement in sensibility, gradation, and stability with the passage of time and amelioration of low illuminance non-** is indicated.

[0016] Moreover, the silver halide emulsion with which low intensity reciprocity law failure was improved is indicated, without reducing inside illuminance sensibility to the Europe patent No. 336,427 and JP,2-20852,A with the vanadium, the chromium, the manganese, the iron, the ruthenium, the osmium, rhenium, and iridium metal complex of 6 coordination containing nitrosyl or a thio nitrosyl ligand.

[0017] Furthermore, sensibility is controlled by the metal complex with which a halogen, nitrosyl, thio nitrosyl, cyanogen, water, and thiocyanogen were together put for the ligand of the rhenium complex of 6 coordination by the Europe patent No. 336,689 and JP,2-20855,A, and the emulsion with which low intensity reciprocity law failure was improved is indicated.

[0018] It is indicated that the emulsion which contains the transition metal complex whose two ligands of a 6 coordination metal complex are oxygen inside at JP,3-118535,A in the transition metal complex whose one ligand of a 6 coordination metal complex is carbonyl, and 3-118536 is effective about the photograph engine performance.

[0019] 8 group metal complex of 6 coordination which has at least four cyanogen ligands is contained in *****, and it is indicated by U.S. Pat. No. 5,132,203 that the plate-like particle which does not contain said complex in a 20-350A particle surface layer is high sensitivity. Furthermore, the silver halide emulsion which doped the 6 cyano iron complex to *****, and did not contain this complex in a 20-

350A particle surface layer, and added and carried out the color sensitizing of the feeling coloring matter of ** to the Europe patent No. 508,910 is indicated. In these patents, although it made it higher [sensibility] for 6 cyano complexes to exist near the particle front face, not making it better [to exist in a particle front face] is indicated. That is, in case a 6 coordination cyano metal complex is doped to a particle, the dope location has good ***** of a silver halide particle, but when a complex exists in the front face itself, about the approach of obtaining high sensitivity, it is not indicated at all.

[0020] The cyanogen generated by the interaction of 6 coordination cyano metal complex and gelatin forms golden ion and a stable golden cyanogen complex, and exists in stability in an emulsion medium. For this reason, sufficient sensibility had not been obtained, although 6 coordination cyano metal complex had been doped by ***** of a silver halide particle since it became difficult to already stick to golden ion on a particle front face and the photograph effectiveness by chemical sensitization fell.

[0021] In JP,6-242537,A, the effectiveness is pulled out to the maximum extent, making this complex exist in a particle front face by making the value of pH a silver halide 7.0 or more in the process which dopes 6 coordination cyano metal complex in some or all in a dope. The method of obtaining high sensitivity is indicated by JP,6-289512,A by making the process which dopes 6 coordination cyano metal complex to a silver halide and the gelatin (for example, FUTARU-ized gelatin, esterification gelatin) which made the amino group or a carboxyl group the invalid after it, or oxidation-treatment gelatin exist. The method of carrying out particle formation to JP,8-29905,A under existence of the compound with which a silver halide particle checks the reaction of gelatin and a cyano complex, for example, zinc, caesium, copper, lead, calcium, barium, or the salt of magnesium, and obtaining high sensitivity is indicated.

[0022] The method of making JP,2-234351,A contain polyvalent metal ion in a part or all of a silver halide particle at homogeneity, and acquiring high sensitivity low fogging in a large illuminance region is indicated.

[0023] Moreover, the approach of increasing low illuminance non-***** and a photographic speed to JP,8-314043,A and JP,8-328182,A by doping 8 group (Fe, Ru, Os) system dopant and the iridium system dopant of a periodic table to the field to which it differs in a silver halide particle is indicated.

[0024] However, by separating those dope fields using an iridium system dopant and metallic elements other than 8 groups also in which the above-mentioned well-known example, there was no example which indicated the approach of high illuminance non-*****, and it was still inadequate also about high-sensitivity-izing of a silver halide emulsion.

[0025]

[Problem(s) to be Solved by the Invention] The purpose of this invention is by making the field to which silver halide particles differ contain the metallic-compounds dopant which consists of a complex centering on a kind of metal of the 7th group or the 9th group to the 14th group, or its metal ion itself at least from the 3rd group of the 4th, 5, and 6 period of an iridium system dopant and the periodic table to offer high illuminance non-***** and/or the silver halide emulsion formed into high sensitivity-low fogging, and silver halide photosensitive material.

[0026]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the item shown below.

[0027] (1) The silver halide emulsion characterized by containing the silver halide particle from which a silver halide particle contains combining the metallic-compounds dopant and iridium system compound dopant which are a complex centering on a kind of metal of the 7th group or the 9th group to the 14th group, or its metal ion at least from the 3rd group of the 4th, 5, and 6 period of the periodic table, and the iridium system compound dopant content section in a particle and the metallic-compounds dopant content section differ.

[0028] (2) Said silver halide emulsion of 1 characterized by making a silver halide fine grain emulsion contain the iridium system compound dopant contained in a silver halide particle, adding, and carrying out deposition to a silver halide particle.

[0029] (3) the silver halide photosensitive material with which the silver halide emulsion of this

photosensitive layer which boils further and is contained at least is characterized by being the silver halide emulsion of said 1 or 2 publications in the silver halide photosensitive material which has the photosensitive layer which contains a kind of silver halide particle at least on a base material.

[0030] Explanation detailed about this invention is described below. General investigation of the iridium system dopant used for the purpose of/ or others in order to reduce reciprocity law failure is Photographic. Science and It is indicated by Engineering, Vol.24, No.6, Nov/Dec1980, and pp 265-267. Still more general investigation of the dopant for reducing reciprocity law failures including an iridium system dopant is Research. Disclosure, Vol.365, Sep It is indicated by the denaturation conditions of 1994, Item36544, a SectionI emulsion particle and its preparation, and a SectionD particle, and accommodation. Although the cause that a high sensitivity photographic emulsion is obtained by this invention is not certain, the following presumed devices can be considered as one explanation.

[0031] It is thought that an iridium system dopant generally acts as a deep electron trap. On the other hand, the dopant centering on metals other than 8 groups of this invention doped in the silver halide emulsion particle gives a shallow electron trap compared with an iridium system dopant. This is because the lowest unoccupied molecular orbital (LUMO) of the dopant of this invention comes to exist near the conduction band (CB) of a silver halide. In the emulsion particle by which the dopant of this invention was doped, a photoelectron is temporarily captured by this shallow electron trap.

[0032] If light is absorbed by the particle, the pair of an electron hole and an electron is formed and an electron can move about the inside of the crystal structure of a particle freely. A cyano ligand tends to give an electron trap with it, therefore tends to give a high sensitivity emulsion. [large ligand field fission and] [shallow] Also in the emulsion particle by which the metal complex of this invention was doped, since selection of a ligand can give the function of a shallow electron trap, a photoelectron is temporarily captured by this shallow electron trap. When a shallow electron trap exists in high concentration like this invention, even if an electron comes out of a shallow electron trap, the probability captured by the shallow electron trap which is in near again is high. Thus, coming out of a shallow trap or entering, a photoelectron becomes possible [having a comparatively long time amount life], and can gather the probability which contributes to silver-nucleus formation, i.e., latent-image formation, by this. Thus, the sensibility of an emulsion can be made to increase by stopping an electron in a particle for latent-image formation.

[0033] However, high illuminance non-** was not improved but the conventional dope emulsion of photographic sensitivity was inadequate.

[0034] for example, although the part or the method of boiling all, making homogeneity contain polyvalent metal ion, and acquiring high sensitivity low fogging in a large illuminance region of a silver halide particle is indicated by JP,2-234351,A, when a shallow electron trap and a comparatively deep electron trap contain in the same phase, the effectiveness of a shallow electron trap disappears and there is a possibility that high sensitivity-ization may not be attained, much.

[0035] Moreover, although the approach of increasing low illuminance non-***** and a photographic speed to JP,8-314043,A and JP,8-328182,A by doping 8 group (Fe, Ru, Os) system dopant and the iridium system dopant of a periodic table to the field to which it differs in a silver halide particle is indicated, high illuminance amelioration is not touched on but high-sensitivity-izing is also still inadequate.

[0036] In this invention, high illuminance amelioration and high sensitivity-ization are attained to coincidence by doping the metal complexes or the metal ions itself other than 8 groups who give the iridium system dopant which gives a comparatively deep electron trap, and a shallow electron trap to the field to which it differs in a particle.

[0037] The central metal or metal ion of a complex which constitutes the metallic-compounds dopant contained to a silver halide particle in this invention It is desirable to consist of the element of the 9th group to the 13th group of the 4th, 5, and 6 period of the periodic table, it is more desirable to consist of the element of the 9th group of the 4th, 5, and 6 period or the 13th group further, and it is most desirable to consist of the element (Ga, In, Tl) of the 13th group of the 4th, 5, and 6 period.

[0038] Although it can select independently respectively as a ligand of the complex which constitutes

the metallic-compounds dopant contained to a silver halide particle in this invention, at least four of all ligands are an anionic ligand, and it is [a piece at least] desirable to show electronic suction nature higher than halogenide ion.

[0039] the general appraisal method of electronic suction nature -- Inorganic Chemistry: Principles of Structure and Reactivity (James E. Huheey, 1972, Harper and Row, New York) -- and -- Absorption Spectra and Chemical Bonding in Complexes (C. K. Jorgensen, 1962, Pergamon Press, London) It is indicated.

[0040] The effectiveness of a ligand when giving electronic suction nature from these reference improves as the coordination atom combined with the metal changes with $\text{Cl} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{N} \rightarrow \text{C}$. For this reason, CN, -, CO are especially suitable ligands. As other suitable ligands, thiocyanate (NCS-), selenocyanate (NCSe-), cyanate (NCO-), TERURO cyanate (NCTe-), and azide (N₃-) are mentioned.

[0041] In addition, it can choose from each various ligand forms indicated by McDugle's and others U.S. Pat. No. 4,933,272, 4,981,781 and 5,037,732, Marchetti's and others U.S. Pat. No. 4,937,180, and Keevert's and others U.S. Pat. No. 5,037,732 list as an example of the ligand which can be used at Olm's and others U.S. Pat. No. 5,360,712.

[0042] As a concrete example of the metallic-compounds dopant used for this invention ** CdBr₂, CdCl₂, and Cd(NO₃) two -- ZnCl -- two -- InCl -- three -- Ga(NO₃) -- three -- TiCl -- three -- TiCl -- Pb(NO₃) -- two -- K -- four -- Re -- (-- CN --) -- six -- K -- four -- Rh -- (-- CN --) -- six -- K -- four -- Re(bpy) -- (-- CN --) -- five -- K -- four -- Rh(SCN) -- (-- CN --) -- five -- K -- four -- Re -- (-- CN --) -- five (OCN) -- K -- four -- Rh -- (-- CO --) -- (-- CN --) -- five -- K -- four -- Re -- (-- CN --) -- five (SCN) -- K -- four -- Rh -- (-- CN --) -- five (N₃) -- K₄Re(CN)₅Cl, K₄Rh(CN)₅Cl, etc. are mentioned. Moreover, a central metal is able to use the complex contained in the 7th group or the 14th group from the 9th group from the 3rd group of the 4th, 5, and 6 period of the periodic table among the metal complexes which contain in Japanese Patent Application No. 9-263826 and Japanese Patent Application No. 9-357173 the ligand which has an adsorption radical to the silver halide of a publication.

[0043] It is built in the crystal-lattice structure of a particle in the form of the six-coordinate complex which uses Ir as a central metal preferably as a dope gestalt which an iridium system dopant contains to a silver halide particle in this invention, and four or more of six ligands are a halogenide system anion, and they are most preferably built in in the form of 3(IrBr₃)- or (IrCl₃) 3-.

[0044] When the most, make it more desirable, although not decided uniformly to contain an iridium system dopant in the interior side of a particle that whether you make which of an iridium system dopant and a metallic-compounds dopant contain in the interior side of a particle about a dope field should just choose the more desirable one according to the iodine presentation of a particle etc.

[0045] Although it is not necessary to necessarily prepare the staging area containing neither of the dopants between each dope fields about dividing a dope field, it is desirable to prepare the staging area of 50% or less 5% or more of the total silver content of one particle, and it is more desirable to prepare the staging area of 40% or less 10% or more of the total silver content of one particle.

[0046] An iridium system dopant and a metallic-compounds dopant are desirable, and the concentration of a dopant is 5×10^{-5} to 1×10^{-4} mol per one mol of silver more preferably 1×10^{-8} to 5×10^{-3} mol per one mol of silver of a particle.

[0047] Next, the silver halide particle used for this invention is explained. The silver halide particles of this invention are a silver bromide, a silver chloride, silver iodide, a salt silver bromide, salt silver iodide, iodine silver bromide, and salt iodine silver bromide. The other silver salt, for example, rhodan silver, a silver sulfide, silver selenide, silver carbonate, silver phosphate, and organic-acid silver may be contained as another particle or a part of silver halide particle. When speeding up of development, desilvering, and a process (bleaching, fixing, and bleaching fixing) is desired, a silver halide particle with many silver chloride contents is desirable. Moreover, when making development control moderately, it is desirable to contain silver iodide. A desirable silver iodide content changes with target sensitive material. For example, in a X-ray sensitized material, it is the range where 0.1-5-mol % is desirable in % and graphic 0.1-15-mol arts and a micro sensitized material. the silver halide particle which contains 1 - 30% of silver iodide preferably in the case of the photography sensitized material

represented by the color negative -- it is -- further -- desirable -- 5-20-mol % -- it is 8-15-mol % especially preferably. It is desirable to make an iodine-silver-bromide particle contain a silver chloride, when making a grid strain ease.

[0048] As for the silver halide particle of this invention, it is desirable to have distribution or structure about a halogen presentation in the particle. The typical thing is the particle of the core shell mold which has the halogen presentation from which the interior and the surface of a particle which is indicated by JP,43-13162,B, JP,61-215540,A, 60-222845, 60-143331, 61-75337, etc. differ, or a duplex structured type. Moreover, it can be made not mere dual structure but the Mie structure which is indicated by JP,60-222844,A, or the multilayer structure beyond it, and the silver halide which has a presentation which is different on the front face of the particle of the dual structure of a core shell can be attached thinly.

[0049] In the case of the silver halide with which two or more silver halides exist with the structure as mixed crystal, it is important to control the halogen presentation distribution between particles. The measuring method of the halogen presentation distribution between particles is indicated by JP,60-254032,A. It is a desirable property that the halogen distribution between particles is uniform. The high emulsion of especially the homogeneity of 20% or less of coefficient of variation is desirable. Another desirable gestalt is an emulsion which has correlation in grain size and a halogen presentation. An iodine content is as high as a large size particle as an example, and, on the other hand, smaller size is the case where there is correlation which is low. Reverse correlation and correlation by other halogen presentations can be chosen for the purpose. It is desirable to mix two or more emulsions with which presentations differ for this purpose.

[0050] It is important to control the halogen presentation near the front face of a silver halide particle. The silver iodide content near the front face is made high, or since adsorbent [of coloring matter] and a development rate are changed, to make a silver chloride content high can be chosen according to the purpose. When changing the halogen presentation near the front face, both of structure which make it adhere to a part of particle can be chosen also with the structure of wrapping in the whole particle. For example, (100), only one field of 14 face-piece particle which consists of a field and a field (111) changes a halogen presentation, or it is the case where one halogen presentation of the principal plane of a monotonous particle and a side face is changed.

[0051] Also by normal ** which does not contain a twin plane, the silver halide particle of this invention can be chosen and used according to the purpose from the volume foundation of edited by Society of Photographic Science and Technology of Japan and photograph industry, and on film photo (Corona Publishing) and an example which is explained to P.163, for example, the single twin crystal containing one twin plane, the parallel multiplex twin crystal containing two or more parallel twin planes, the unparallel multiplex twin crystal containing two or more twin planes [**** / un-], etc. Moreover, although the example which mixes the particle from which a configuration differs is indicated by U.S. Pat. No. 4,865,964, this approach can be chosen as occasion demands. In normal ** (100), 12 face-piece particle which consists of a field currently indicated by the cube which consists of a field, the octahedron which consists of a field (111), JP,55-42737,B, and JP,60-222842,A (110) can be used. furthermore, Journal of Imaging it is reported in Science, 30 volumes, 247 pages, and 1986 -- as (211) -- although the method of preparation also takes a device to the field particle which makes representation the field particle made into representation (hll), the field particle which makes (331) representation (hhl), the field particle which makes a field (210) representation (hk0), and a field (321) (hkl), it can choose and use according to the purpose. (100) Particles with which two fields or many fields coexist, such as 14 face-piece particle with which a field and a field (111) coexist to one particle, and a particle with which a field (100) and a field (110) coexist, can also be chosen and used according to the purpose. The configuration of an aspect ratio, a call, and a plate-like particle is specified for the value which broke the circle equivalent diameter of the photographed area of a particle by particle thickness. The plate-like particle with a larger aspect ratio than 1 can be used as a silver halide particle of this invention. A plate-like particle The Kleave work "as actual as the theory of a photograph" (Cleve, Photography Theory and Practice (1930)), 131 pages; Gutoff work and photograph GURAFIKU Science - and - engineering

(Gutoff, Photographic Science and Engineering), It can prepare by the approach of a publication to the 14th volume, U.S. Pat. No. 4,434,226, 4,414,310, 4,433,048, 4,439,520, the British patent No. 2,112,157, etc. [248-257 pages (1 970 years);] When a plate-like particle is used, there are advantages, like that covering power is improved and the color-sensitizing effectiveness by sensitizing dye increases, and it is stated to U.S. Pat. No. 4,434,226 quoted previously in detail. As 80% or more of an average aspect ratio of a total projected area of a particle, 100 or less [1 or more] are desirable. It is 20 or less [2 or more] more preferably, and is zero or less [three or more] especially preferably. Since a pressure drop etc. will be produced if an aspect ratio becomes high too much, it is not desirable. A triangle, a hexagon, a round shape, etc. can be chosen as a configuration of a plate-like particle. The forward hexagon with almost equal die length of six sides which is indicated by U.S. Pat. No. 4,797,354 is a desirable gestalt.

[0052] Although the circle equivalent diameter of the projected area of a particle is used as a grain size of a plate-like particle in many cases, a particle 0.6 micrometers or less has a desirable average diameter which is indicated by U.S. Pat. No. 4,748,106 for high-definition-izing. Moreover, it is desirable to limit more preferably 0.5 micrometers or less of particle thickness to 0.3 micrometers or less as a configuration of a plate-like particle, when raising sharpness. The particle which specified the thickness of a particle and the face to face dimension of a twin plane which are furthermore indicated by JP,63-163451,A is also desirable.

[0053] Moreover, when a mono dispersion plate-like particle with narrow grain-size distribution is used, a still more desirable result may be obtained. The manufacturing method of a mono dispersion hexagon-head plate-like particle with the high rate of monotonous-izing is indicated by U.S. Pat. No. 4,797,354 and JP,2-838,A. Moreover, the Europe patent No. 514,742 has the publication about the approach the coefficient of variation of grain-size distribution manufactures less than 10% of plate-like particle using a polyalkylene oxide block copolymer. It is desirable to use these plate-like particles for this invention. Furthermore, a high particle also has [the coefficient of variation of particle thickness] the desirable homogeneity of 30% or less of thickness.

[0054] In the case of a plate-like particle, observation of a dislocation line is **** by the electron microscope of a transparency mold. It is desirable to choose [for the purpose of the particle containing the rearrangement of the particle which does not contain a dislocation line at all, the particle containing several rearrangements, or a large number]. Moreover, or it introduces over the whole particle, for example, it can also choose the rearrangement linearly introduced to the specific direction of the crystal orientation of a particle, or the curved rearrangement, and it introduces only into the specific part of a particle, it can limit to the fringe section of a particle and can choose from introducing a rearrangement etc. Not only the case of a plate-like particle but in the case of the indeterminate mold particle represented by a normal crystallite child or the potato particle, installation of a dislocation line is desirable. Also in this case, it is a desirable gestalt to limit to specific parts, such as top-most vertices of a particle and **.

[0055] the silver halide particle of this invention -- the Europe patent 96,727BNo. 1 -- said -- reforming of a front face which is indicated by the processing which brings a radius of circle to a particle which is indicated by No. 64,412B1 etc. or the 2,306,447th patent C No. 2 of West Germany, and JP,60-221320,A may be performed.

[0056] Although structure ***** in a particle front face is common, it is desirable by the case to form irregularity deliberately. The method of making a hole in the center of some crystals, for example, top-most vertices, indicated by JP,58-106532,A and 60-221320 or a field or the ruffle particle indicated by U.S. Pat. No. 4,643,966 is the example.

[0057] The circle equivalent diameter of the projected area which used the electron microscope, the ball equivalent diameter of projected area and the particle volume particle thickness Mika computed, or the ball equivalent diameter of the volume by the Coulter counter method can estimate the grain size of the silver halide particle of this invention, and the particle finally obtained. As a ball equivalent diameter, from an ultrafine particle 0.05 micrometers or less, it can choose from the big and rough particles exceeding 10 micrometers, and can use. It is using 0.1-micrometer or more particle 3 micrometers or

less as a photosensitive silver halide particle preferably.

[0058] The silver halide particle or the particle finally obtained of this invention can also choose the so-called polydispersed emulsion with large grain-size distribution, or the narrow mono dispersion emulsion of a size distribution according to the purpose, and can be used. The coefficient of variation of the projected-area equivalent diameter of a particle or the ball equivalent diameter of the volume may be used as a scale showing a size distribution. When using a mono dispersion emulsion, it is good for coefficient of variation to use the emulsion of 15% or less of size distribution still more preferably 20% or less more preferably 25% or less.

[0059] A mono dispersion emulsion may be specified as grain-size distribution to which 80% or more of all particles go into less than **30% of average grain size by the particle number or weight. Moreover, in order for sensitive material to satisfy target gradation, multistory spreading of two or more sorts of mono dispersion silver halide emulsions with which grain size differs in the emulsion layer which has the same color sensitivity substantially can be carried out in mixing or another layer at the same layer. The combination of two more or more kinds of polydispersed silver halide emulsions or a mono dispersion emulsion, and a polydispersed emulsion can also be used mixing or carrying out multistory.

[0060] The silver halide particle of this invention The Glafkides work "the physics of a photograph, and chemistry", Pole MONTERU Co. ** (P. Glafkides, Chimie et Physique Photographique Paul Montel, 1967), the Duffin work "photographic-emulsion chemistry" and the Focal Press Co. ** (G. -- F.Duffin and Photographic Emulsion Chmistry [(Focal Press, 1966)] --) Work, such as ZERIGUMAN "manufacture of a photographic emulsion, and spreading", It can prepare using the approach indicated by the Focal Press Co. ** (V. L.Zelikman etal, Making and Coating Photographic Emulsion, Focal Press, 1964) etc. That is, both acid process a neutral process the ammonia method, etc. are good, and any, such as single-sided alligation, coincidence alligation, and those combination, may be used as a format of making fusibility silver salt and fusibility haloid salt reacting. The approach (the so-called back-mixing method) of making a particle forming in the bottom of overcomplex ion can also be used. The approach of keeping constant pAg in the liquid phase which a silver halide particle generates as one format of coincidence alligation, i.e., the so-called conte RORUDO TABURU jet process, can also be used. According to this approach, crystal form is regular and a silver halide particle with the grain size near homogeneity is obtained.

[0061] It is effective, also when the approach of adding the silver halide particle which carried out precipitate formation beforehand in the reaction container for emulsion preparation, U.S. Pat. No. 4,334,012, 4,301,241, and 4,150,994 are desirable, these can be used as seed crystal by the case and it supplies as a silver halide for growth. It is desirable, and it can distribute to whole-quantity addition and multiple times at once as the addition approach, and adding an emulsion with a small grain size in the case of the latter can choose from addition, adding continuously, etc., and it can use. Moreover, in order to carry out reforming of the front face, it is also effective by the case to add the particle of various halogen presentations.

[0062] Most or the approach of transforming a part with a halogen transformation method very much of a halogen presentation of a silver halide particle is indicated by U.S. Pat. No. 3,477,852, 4,142,900, the Europe patent No. 273,429, 273,430, the West German public presentation patent No. 3,819,241, etc., and is the effective particle forming method. Although changed into more poorly soluble silver salt, the solution or silver halide particle of a fusibility halogen can be added. It can choose out of the approach of dividing, changing or changing into multiple times continuously changed at once.

[0063] Concentration is changed or the particle forming method for changing the rate of flow is a desirable approach as the British patent No. 1,469,480, U.S. Pat. No. 3,650,757, and 4,242,445 indicate particle growth in addition to the approach of adding fusibility silver salt and haloid salt by fixed concentration and the fixed rate of flow. Concentration can be made to be able to increase or the amount of silver halides to supply can be changed by making the rate of flow increase with the linear function of addition time amount, a quadratic function, or a more complicated function. Moreover, it is also desirable by the case to decrease the quantity of a supply silver halide as occasion demands. When adding two or more fusibility silver salt from which a solution presentation furthermore differs or adding

two or more fusibility haloid salt with which solution presentations differ, an addition method which makes one side increase and decreases another side is also an effective approach.

[0064] The mixer at the time of making the solution of fusibility silver salt and fusibility haloid salt react can be chosen from the approaches indicated by U.S. Pat. No. 2,996,287, 3,342,605, 3,415,650, 3,785,777, the West German public presentation patent No. 2,556,885, and 2,555,364, and can be used.

[0065] A silver halide solvent is useful to the purpose which promotes aging. For example, making the halogen ion of an excessive amount exist in promoting aging in a reactor is known. Moreover, other aging agents can also be used. These aging agents can also be introduced into a reactor while they can blend the whole quantity into the dispersion medium in a reactor and add a halogenide salt, silver salt, or a deflocculant, before they add silver and a halogenide salt. As another deformation mode, an aging agent can also be introduced independently in a silver halide salt and a silver salt addition phase.

[0066] as an aging agent -- ammonia and a thiocyanate (for example, a potassium rhodanide --) rhodan ammonium and an organic thioether compound (for example, U.S. Pat. No. 3,574,628 --) 3,021,215, 3,057,724, 3,038,805, 4,276,374, 4,297,439, 3,704,130, A compound given in 4,782,013, JP,57-104926,A, etc., a thione compound (for example, JP,53-82408,A and 55-77737 --) The 4 permutation thiourea indicated by U.S. Pat. No. 4,782,013 etc., The compound indicated by JP,53-144319,A, a melt KAPUTO compound, amine compounds (for example, JP,54-100717,A etc.) which can promote growth of the silver halide particle indicated by JP,57-202531,A, etc. are raised.

[0067] Although it is advantageous to use gelatin as the protective colloid used at the time of preparation of the emulsion of this invention, and a binder of other hydrophilic colloid layers, the other hydrophilic colloid can also be used.

[0068] For example, a gelatin derivative, the graft polymer of gelatin and other macromolecules, Albumin, protein like casein; Hydroxyethyl cellulose, A carboxymethyl cellulose, the **** cellulosic of cellulose sulfates, Sodium alginate, a sugar derivative like a starch derivative; Polyvinyl alcohol, A polyvinyl alcohol partial acetal, Poly N-vinyl pyrrolidone, A single like polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, and a polyvinyl pyrazole or the synthetic hydrophilic-property high polymer of the variety like a copolymer can be used.

[0069] Enzyme processing gelatin which was indicated by acid-treatment gelatin besides liming gelatin and Bull.Soc.Sci.Photo.Japan.No.16.P30 (1966) as gelatin may be used, and the hydrolyzate and the enzyme decomposition product of gelatin can also be used.

[0070] As for the emulsion of this invention, it is desirable to make it the protective colloid distribution which rinsed for demineralization and was prepared newly. Although the temperature of rinsing can be chosen according to the purpose, it is desirable to choose in 5 degrees C - 50 degrees C. Although pH at the time of rinsing can also be chosen according to the purpose, choosing between 2-10 is desirable. It is the range of 3-8 still more preferably. Although pAg at the time of rinsing can also be chosen according to the purpose, choosing between 5-10 is desirable. It can choose from the dialysis using the noodle rinsing method and semipermeable membrane as the approach of rinsing, a centrifuge method, a coagulation sedimentation method, and an ion-exchange method, and can use. In the case of a coagulation sedimentation method, it can choose out of the approach of using a sulfate, the approach using an organic solvent, the approach using a water-soluble polymer, the approach using a gelatin derivative, etc.

[0071] The approach of adding a chalcogenide compound which is indicated by U.S. Pat. No. 3,772,031 during emulsion preparation may also be useful. A cyanogen salt, a thiocyanogen salt, a seleno cyanic acid, a carbonate, phosphate, and acetate may be made to exist besides S, Se, and Te.

[0072] the silver halide particle of this invention -- at least one of sulfur sensitization, selenium sensitization, gold sensitization, palladium sensitization, or the noble-metals sensitization -- the process of the arbitration of the production process of a silver halide emulsion -- ***** -- things are made. It is desirable to combine two or more sorts of sensitization methods. The emulsion of various types can be prepared by at which process chemical sensitization is carried out. There is a type by which a chemical sensitization nucleus is buried inside a particle, a type buried in a location shallow from a particle front face, or a type which makes a chemical sensitization nucleus on a front face. Generally the emulsion of

this invention is the case which can choose the location of a chemical sensitization nucleus according to the purpose where desirable one makes a kind of chemical sensitization nucleus at least near the front face.

[0073] One of the chemical sensitization which can be preferably carried out by this invention is independent or the combination of chalcogenide sensitization and noble-metals sensitization. The James (T. H. James) work, a THE photographic process, the 4th edition, the Macmillan Co. **, and 1977 (it James(es) T. -- H. --), The Theory of the Photographic Process, 4th Can carry out using active gelatin so that it may be indicated by ed, Macmillan, and 1977 67-76 page, and Moreover, 120 research disclosure, April, 1974, 12008; Research disclosure, 34 volumes, June, 1975, 13452, U.S. Pat. No. 2,642,361, 3,297,446 -- said -- the 3rd, and 773 or 031. No. and 3,857,711 -- 3,901,714, 4,226,018, and 3,904,415, In pAg 5-10, pH 5-8, and the temperature of 30-80 degrees C, it can consider as two or more combination of sulfur, a selenium, a tellurium, gold, platinum, palladium, or these sensitizers so that it may be indicated by the list at the British patent No. 1,315,755. In noble-metals sensitization, for example, ***** of gold, platinum, and palladium can be used, and concomitant use of gold sensitization, palladium sensitization, and both is desirable also in especially inside. In the case of gold sensitization, chloroauric acid, a potassium clo ROO rate, kalium aurithiocyanate, a gold sulfide, and the well-known compound of golden SERENAIDO can be used. A palladium compound means a palladium divalent salt or a tetravalent salt. A desirable palladium compound is expressed with M_2PdX_6 or M_2PdX_4 . M expresses a hydrogen atom, an alkali-metal atom, or ammonium here. X expresses a halogen atom and expresses chlorine, a bromine, or an iodine atom.

[0074] Specifically, K_2PdCl_4 , $2(NH_4)PdCl_6$, Na_2PdCl_4 , $2(NH_4)PdCl_4$, Li_2PdCl_4 , Na_2PdCl_6 , or K_2PdBBr_4 is desirable. As for a gold compound and a palladium compound, using together with a thiocyanate or selenocyanate is desirable.

[0075] As a sulfur sensitization agent, the sulfur content compound indicated by a hypo, a thiourea system compound, a rhodanine system compound and U.S. Pat. No. 3,857,711, 4,226,018, and 4,054,457 can be used. Chemical sensitization can also be carried out to the bottom of existence of the so-called chemical sensitizer. The compound known as a thing like an aza-indene, aza-pyridazine, and an aza-pyrimidine which controls a fogging in process of chemical sensitization, and increases sensibility is used for a useful chemical sensitization assistant. The example of a chemical sensitization assistant modifier is indicated by U.S. Pat. No. 2,131,038, 3,411,914, 3,554,757, JP,58-126526,A and the above-mentioned Duffin work "photographic-emulsion chemistry", and 138-143 pages.

[0076] As for the emulsion of this invention, it is desirable to use gold sensitization together. It is 1×10^{-4} to 1×10^{-1} ten - seven mols per one mol of silver halides as a desirable amount of a gold sensitization agent, and 1×10^{-5} to 5×10^{-1} ten - seven mols are still more desirable. The desirable range of a palladium compound is 1×10^{-3} to 5×10^{-7} . The desirable range of a thiocyanogen compound or seleno cyanides is 5×10^{-2} to 1×10^{-6} .

[0077] The desirable sulfur sensitization dose used to the silver halide particle of this invention is 1×10^{-4} to 1×10^{-1} ten - seven mols per one mol of silver halides, and 1×10^{-5} to 5×10^{-7} mol is still more desirable.

[0078] There is selenium sensitization as a desirable sensitization method to the emulsion of this invention. Specifically in selenium sensitization, a selenium compound like a colloid metal selenium, selenourea, seleno ketones (for example, N and N-dimethyl selenourea, N, and N-diethyl selenourea etc.), and seleno amides can be used using a well-known unstable selenium compound. It may be more desirable to use selenium sensitization combining sulfur sensitization, ***** sensitization, or its both.

[0079] Moreover, as for the emulsion of this invention, reduction sensitization may be given. As a reduction sensitization method which can be used, it is Photographic, for example. Various kinds of reduction sensitization methods are shown in the publication of Sensitivity (through Tadaaki work, Oxford University Press 1995) from 180 pages. However, the technique of reduction sensitization is not limited to a ***** cage and these. that is, it is made to grow up in the ambient atmosphere of low pAg of pAg 1-7 called the approach of adding a well-known reducing agent, and silver aging to a silver halide emulsion -- it is -- it is -- it is made to grow up in the ambient atmosphere of high pH of the approach of ripening, and pH 8-11 called high pH aging as shown in JP,10-26810,A -- it is -- it is -- the

approach of ripening etc. is learned and two or more approaches can also be used together. The approach of adding a reduction sensitization agent is a desirable approach at the point that the level of reduction sensitization can be adjusted delicately.

[0080] Stannous salt, an amine and a polyamine acid, a hydrazine derivative, formamidinesulfinic acid, a silane compound, a borane compound, etc. are well-known as a reduction sensitization agent. It can be chosen as this invention out of these well-known compounds, and can also use for it. Moreover, two or more sorts of compounds can also be used together. Stannous chloride, a thiourea dioxide, and dimethylamine borane are desirable compounds as a reduction sensitization agent. The alkynyl amine compound of a publication can be chosen as U.S. Pat. No. 5,389,510 still more preferably. Although it is necessary to choose an addition since it depends for the addition of a reduction sensitization agent on emulsion manufacture conditions, the range of 10⁻⁷ to ten⁻³ mols per one mol of silver halides is suitable. Moreover, an ascorbic acid and its derivative can also be used as a reduction sensitization agent.

[0081] the addition for which, as for the ascorbic-acid compound, the reduction sensitization agent is used preferably conventionally -- comparing -- **** for large quantities -- things are desirable. JP,57-33572,B "lessons is usually taken for the amount of a reducing agent from complex ion g, and it does not exceed 0.75x10⁻² to 2 milliequivalent (8x10⁻⁴ mols /, AgX mol). It is effective when the amount (10 as an ascorbic acid -7 - 10⁻⁵ mols /, AgX mol) of 0.1-10mg per silver nitrate kg is many. (A reduced property is based on artificers) It is described as ". "It is 1x10⁻⁷ to 44xten⁻⁶ mols as an addition which can use a tin compound as a reduction sensitization agent" is indicated by U.S. Pat. No. 2,487,850. Moreover, it is indicated that it is appropriate to use about 0.01mg - about 2mg per one mol of silver halides as an addition of a thiourea dioxide, and to use about 0.01mg - about 3mg for JP,57-179835,A as stannous chloride. Although a desirable addition depends for the ascorbic-acid compound used for this invention according to factors, such as temperature of the grain size of an emulsion, a halogen presentation, and emulsion preparation, and pH, pAg, it is desirable to choose out of the range of 5x10⁻⁵ to 1xten⁻¹ mol per one mol of silver halides. It is desirable to choose out of the range of 5xten⁻⁴ - four mols - 1xten⁻¹ - two mols still more preferably. Especially a desirable thing is choosing out of the range of 1xten⁻¹ - three mols - 1xten⁻¹ - two mols.

[0082] A reduction sensitization agent can be melted to solvents, such as water or alcohols, glycols, ketones, ester, and amides, and can be added during particle formation, before chemical sensitization, or to the back. Although you may add in process of [any] an emulsion production process, especially a desirable thing is the approach of adding during particle growth. Although it is also good to add in a reaction container beforehand, to add at the suitable stage of particle formation is more desirable. Moreover, the reduction sensitization agent is beforehand added in the water solution of water-soluble silver salt or water-soluble alkali halide, and particle formation may be carried out using these water solutions. Moreover, even if it adds the solution of a reduction sensitization agent in several steps with particle formation, a desirable approach also carries out long duration addition continuously.

[0083] The photographic emulsion used for this invention can be made to contain various compounds in order to prevent the fogging under the production process of sensitive material, preservation, or photographic processing or to stabilize the photograph engine performance. Namely, thiazoles, for example, a benzo thiazolium salt, and nitroimidazoles, Nitrobenzimidazole, chloro benzimidazole, and BUROMO benzimidazole Mercapto thiazoles, mercaptobenzothiazoles, and mercapto benzimidazole Mercapto thiadiazole, aminotriazoles, and ** NZOTORI azoles Nitro ** NZOTORI azoles and mercaptotetrazoles (especially 1-phenyl-5-mercapto tetrazole); mercaptopyrimidine; mercapto triazine; for example A thio keto compound like oxazoline thione; Aza-indenes For example, many compounds known as the antifogging agent [like] which are TORIAZA indenenes, tetraaza indenenes (especially 4-hydroxy permutation (1, 3,a [3], 7) tetraaza indenenes), and pentaazaindene, or a stabilizer can be added. For example, what was indicated by U.S. Pat. No. 3,954,474, 3,982,947, and JP,52-28660,B can be used. There is a compound indicated by one of the desirable compounds at JP,63-212932,A. An antifogging agent and a stabilizer can be added before particle formation, during particle formation, and after particle formation at various stages in front of chemical sensitization, in chemical sensitization,

after chemical sensitization, and before spreading according to the purpose at the time of the distribution after a rinsing process and rinsing. It can use for multiple purposes controlling the array [which controls chemical sensitization] of coloring matter which controls **** of a particle besides adding during emulsion preparation and discovering original fogging prevention and a stabilization effect, which makes grain size small, which decreases the solubility of a particle etc.

[0084] Also as for the photographic emulsion which there is methine coloring matter as spectral sensitization coloring matter made to stick to the silver halide particle of this invention, therefore is finally obtained again, it is desirable that spectral sensitization is carried out by methine coloring matter and others, although the effectiveness of this invention is demonstrated. the coloring matter used -- cyanine dye, merocyanine coloring matter, compound cyanine dye, compound merocyanine coloring matter, and Jolo Pau Ra cyanine dye -- passing -- MISHIANIN coloring matter and styryl coloring matter -- and it passes and MIOKISO Norian coloring matter is included. Especially useful coloring matter is cyanine dye, merocyanine coloring matter, and coloring matter belonging to compound merocyanine ****. All of the nucleus usually used for cyanine dye as a basic heterocycle nucleus are applicable to these coloring matter. Namely, for example, a pyrroline nucleus, an oxazoline nucleus, a thio ZORIN nucleus, a pyrrole nucleus, An oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, A tetrazole nucleus, a pyridine nucleus; The nucleus which the aromatic hydrocarbon ring ****(ed) in nucleus; which the alicyclic hydrocarbon ring united with these nuclei, and these nuclei, That is, for example, an India renin nucleus, a ** NZUINDO renin nucleus, the Indore nucleus, a benzoxazole nucleus, a naphth oxazole nucleus, a benzothiazole nucleus, a naphth thiazole nucleus, benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus are applicable. These nuclei may be permuted on the carbon atom.

[0085] A 5 - 6 member heterocycle nucleus like a pyrazoline-5-ON nucleus, a thiohydantoin nucleus, 2-thio KISAZO lysine -2, 4-dione nucleus, thiazolidine -2, 4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus as a nucleus which has keto methylene structure is applicable to merocyanine coloring matter or compound merocyanine coloring matter.

[0086] Although these sensitizing dye may be used independently, those combination may be used and the combination of sensitizing dye is often especially used for the purpose of a strong color sensitizing. The example of representation U.S. Pat. No. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, It is indicated by 4,026,707, the British patent No. 1,344,281, 1,507,803, JP,43-4936,B, 53-12375, JP,52-110618,A, and 52-109925.

[0087] You are the matter which does not absorb substantially the coloring matter or the light which does not have a spectral sensitization operation in itself with sensitizing dye, and the matter in which a strong color sensitizing is shown may also be included in an emulsion.

[0088] The addition stages of the desirable spectral sensitization coloring matter of this invention are after silver halide particle formation and before particle addition. But although carried out ordinarily at the stage of a before [after / completion / spreading of chemical sensitization], in advance of chemical sensitization, it can also perform adding at a chemical-sensitizer and coincidence term and performing spectral sensitization to chemical sensitization and coincidence as indicated by JP,58-113928,A, as indicated by U.S. Pat. No. 3,628,969 and 4,225,666, and it can add before completion of silver halide particle precipitation, and spectral sensitization can also be started. Furthermore, it may also be possible to add to divide said these compounds and to add [a part of], i.e., these compounds, in advance of chemical sensitization as taught to U.S. Pat. No. 4,255,666 again, and to add the remainder after chemical sensitization, and you may be any stage under silver halide particle formation including the approach currently indicated by U.S. Pat. No. 4,183,756.

[0089] Although an addition can be used by 4×10^{-6} to 8xten - three mols per one mol of silver halides, in the case of 0.2-1.2-micrometer more desirable silver halide grain size, about 5×10^{-5} to 2xten - three mols are more effective.

[0090] Although the aforementioned various additives are used in case the emulsion obtained by this invention is used as sensitive material, according to the purpose, various additives can be used besides it.

[0091] These additives are the research disclosure Item in more detail. 17643 (December, 1978), this Item 18716 (November, 1979) and this Item It is indicated by 308119 (December, 1989).

[0092] The silver halide emulsion of this invention can be further used for various photosensitive material by one of the usual approaches. As one important mode, it is suitable to use the silver halide emulsion of this invention for the multilayer photosensitive material which has a two-layer silver halide emulsion layer at least. For example, when it is multilayer photosensitive material like a negative color film and a color reversal film, the silver halide emulsion of this invention may be used for either an upper layer and lower layer side, and may both be used.

[0093]

[Example] Although an example is shown in order to explain this invention more below at a detail, this invention is not limited to them. He can understand this invention better by referring to the example of emulsion preparation which satisfies the requirements for this invention shown below, an emulsion, and a photograph element. sensibility is expressed with the relative value of the logarithm of the inverse number of light exposure E (E -- unit; -- it expresses with lux and a second) which gives the concentration of fogging +0.2.

[0094] By the approach shown below in the example 1 (preparation of the seed emulsion T-1), the seed emulsion T-1 which has the parallel twin plane of two sheets was prepared.

[0095]

(A-1 liquid)

Ossein gelatin 38.0g Potassium bromide 11.7g It is water. 34.0l. (B-1 liquid)

Silver nitrate 810.0g It is water. 3815ml (C-1 liquid)

Potassium bromide 567.3g It is water. 3815ml (D-1 liquid)

Ossein gelatin 163.4g $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_{19.8}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($m+n=9.77$) 10% methanol solution 5.5ml It is water. 3961ml (E-1 liquid)

Sulfuric acid (10%) 91.1ml (F-1 liquid)

56% acetic-acid water solution Initial complement (G-1 liquid)

Aqueous ammonia (28%) 105.7ml (H-1 liquid)

A potassium-hydroxide water solution (10%) Initial complement ($m+n=9.77$) 10% methanol solution 5.5ml With water E-1 liquid is added using stirring equipment given in 3961ml JP,62-160128,A in A-1 liquid violently stirred at 30 degrees C, and it is a double jet process about B-1 liquid and C-1 liquid after that. 279ml was respectively added by fixed speed for 1 minute, and the silver halide nucleus was generated.

[0096] D-1 liquid was added after that, temperature was raised to 60 degrees C over 31 minutes, further G-1 liquid was added, H-1 liquid adjusted pH to 9.3, and aging was performed for 6.5 minutes. Then, F-1 liquid adjusted pH to 5.8, and after that, acceleration addition of the B-1 remaining liquid and the C-1 liquid was carried out in 37 minutes with the double jet process, and it desalted with the conventional method immediately. When this seed emulsion was observed with the electron microscope, it was ECD (projected-area circle conversion particle size) = 0.72micrometer and the COV (particle size distribution) = 16% mono dispersion monotonous kind emulsion which have the parallel twin plane of two sheets mutually.

[0097] (Preparation of comparison emulsion Em-1) Comparison emulsion Em-1 was prepared using the solution indicated below to be the seed emulsion T-1.

[0098]

(A-2 liquid)

Ossein gelatin 519.9g $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_{19.8}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($m+n=9.77$) 10% methanol solution 4.5ml Seed emulsion T-1 5.3 mols It is water. 18.0l. (B-2 liquid)

3.5-N silver-nitrate water solution 2787ml (C-2 liquid)

Potassium bromide 1020g Potassium iodide 29.1g It is water. 2500ml (D-2 liquid)

Potassium bromide 618.5g Potassium iodide 8.7g It is water. 1500ml (E-2 liquid)

Potassium bromide 208.3g It is water. 1000ml (F-2 liquid)

56% acetic-acid water solution Initial complement (H-2 liquid)

From 3.0% of the weight of gelatin, and a silver iodide particle (ECD=0.05micrometer) Fine grain emulsion which changes The method of preparation is shown below by 0.672 mols.

[0099] uniform addition was carried out having poured the water solutions of 3092ml of each which contain a 10.59 mols silver nitrate and a 10.59-mol potassium iodide in 9942ml of 5.0% of gelatin solutions containing a 0.254-mol potassium iodide for 35 minutes, and the particle was formed. The temperature under particle formation was controlled at 40 degrees C, and pH and EAg were taken as the result.

[0100]

(I-2 liquid)

10% potassium-hydroxide water solution Having added A-2 liquid in the initial-complement reaction container, and stirring violently at 75 degrees C, according to the combination which showed B-2 liquid, C-2 liquid, and D-2 liquid in Table 1, it added with coincidence alligation, seed crystal was grown up, and comparison emulsion Em-1 was prepared.

[0101] The addition rate of B-2 liquid, C-2 liquid, and D-2 liquid is changed to the function to addition time amount in consideration of a critical growth rate, and it was made for neither generating of granule children other than a grown-up seed particle nor degradation of the particle size distribution by the Ostwald ripening between growth particles to take place here.

[0102] First, 75 degrees C and pAg were controlled to 8.9, it controlled pH for the solution temperature in a reaction container to 5.8, and crystal growth performed the 1st addition. 65.8% of B-2 liquid was added by this 1st addition. The solution temperature in a reaction container was lowered to 40 degrees C in 30 minutes after that, pAg was adjusted to 10.3, the whole quantity was added for H-2 liquid by fixed speed for 2 minutes, and the 2nd addition was performed immediately. The 2nd addition was performed by having controlled 40 degrees C and pAg to 10.3, and having controlled pH for the solution temperature in a reaction container to 5.0, and added all the remainder of B-2 liquid. For control of pAg and pH, E-2 liquid, F-2 liquid, and I-2 liquid were added if needed.

[0103] After particle formation, according to the approach of a publication, demineralization processing was performed to JP,5-72658,A, and gelatin was added after that, it distributed, and the emulsion of pAg8.06 and pH5.8 was obtained in 40 degrees C. This is set to Em-1.

[0104] When the silver halide particle in this emulsion was observed with the electron microscope, it was the hexagon-head plate-like mono dispersion silver halide particle of ECD=1.50micrometer and the average aspect ratio 7.0 of 14% of particle size distribution.

[0105]

[Table 1]

添加溶液	添加時間 (min.)	添加銀量 (%)	沃化銀含有率 (mol%)	添加区分
B-2, C-2	0.00	0.0	2.0	第1添加
	5.26	1.7	2.0	
	8.63	21.2	2.0	
	12.65	34.8	2.0	
	15.81	47.3	2.0	
	19.85	65.8	2.0	
B-2, D-2	0.00	65.8	1.0	第2添加
	6.23	73.8	1.0	
	12.62	82.5	1.0	
	18.67	91.1	1.0	
	24.42	100.0	1.0	

[0106] (Preparation of comparison emulsion Em-2) Em-2 were prepared by changing the production conditions of [K₂IrCl₆ content] Em-1 as follows. in production of Em-1, when a silver content makes the core of a particle 0%, it contains to 50 - 55% of field -- as -- K₂IrCl₆ -- a water solution -- per [of

the total silver content / 6×10^{-6} mol -six mols added.

[0107] [(Preparation of comparison emulsion Em-3, and 4 and 5) InCl_3 , $\text{Ga}(\text{NO}_3)_3$, $\text{Pb}(\text{NO}_3)_2$ content]

Em-3 and Em-4 were prepared by changing the production conditions of Em-1 as follows. In the phase which consumed 65 to 70 of a silver content% in production of Em-2, the same actuation as preparation of Em-1 was performed except having carried out 4×10^{-6} mol [Ag] addition of InCl_3 , $\text{Ga}(\text{NO}_3)_3$, and $\text{Pb}(\text{NO}_3)_2$ in the water solution, respectively. These emulsions are carried out to Em-3, and 4 and 5, respectively.

[0108] (Preparation of this invention emulsion Em-6, and 7 and 8) [K_2IrCl_6 + InCl_3 , $\text{Ga}(\text{NO}_3)_3$, $\text{Pb}(\text{NO}_3)_2$ content, and staging-area-less]

when a silver content makes the core of a particle 0% in production of Em-1, it contains to 60 - 65% of field -- as -- K_2IrCl_6 -- a water solution -- per [of the total silver content / 6×10^{-6} mol -six mols added. Furthermore, the same actuation as preparation of Em-1 was performed except having carried out 4×10^{-6} mol [Ag] addition of InCl_3 , $\text{Ga}(\text{NO}_3)_3$, and $\text{Pb}(\text{NO}_3)_2$ in the water solution, respectively so that it might contain to 65 to 70 of a silver content%. These emulsions are carried out to Em-6, and 7 and 8, respectively.

[0109] [(This invention emulsion Em- preparation of 9 and 10) K_2IrCl_6 + InCl_3 , $\text{Ga}(\text{NO}_3)_3$ content, 5% of staging areas]

when a silver content makes the core of a particle 0% in production of Em-1, it contains to 55 - 60% of field -- as -- K_2IrCl_6 -- a water solution -- per [of the total silver content / 6×10^{-6} mol -six mols added. Furthermore, the same actuation as preparation of Em-6 was performed except having carried out 4×10^{-6} mol [Ag] addition of InCl_3 and $\text{Ga}(\text{NO}_3)_3$ in the water solution, respectively so that it might contain to 65 to 70 of a silver content%. these emulsions -- respectively -- Em- it is referred to as 9 and 10.

[0110] [(Preparation of this invention emulsion Em-11) K_2IrCl_6 + InCl_3 content, 10% of staging areas] in production of Em-6, it contains to 50 - 55% of field -- as -- K_2IrCl_6 -- a water solution -- per [of the total silver content / 6×10^{-6} mol -six mols added. Furthermore, the same actuation as preparation of Em-6 was performed except having carried out 4×10^{-6} mol [Ag] addition of InCl_3 in the water solution, respectively so that it might contain to 65 to 70 of a silver content%. This emulsion is set to Em-11.

[0111] [(Preparation of this invention emulsion Em-12) K_2IrCl_6 (fine-grain-emulsion addition)+ InCl_3 content, 10% of staging areas]

Fine-grain-emulsion * containing K_2IrCl_6 was added so that the concentration of K_2IrCl_6 might become 6xten - six mols per mol of the total silver content, so that it might contain to 50 - 55% of field of the addition total silver content. Furthermore, the same actuation as preparation of Em-6 was performed except having carried out 4×10^{-6} mol [Ag] addition of InCl_3 in the water solution so that it might contain to 65 to 70 of a silver content%. However, the silver content contained in a fine grain emulsion and the amount of a halogenide were deducted from the original amount, and B-2, C-2, and D-2 were added. This emulsion is set to Em-12.

[0112] The passage of the following [method of preparation / of the process fine grain emulsion of fine-grain-emulsion *]: It added, having poured 2000ml of water solutions which contain a 7.06-mol silver nitrate in 5000ml of 6.0% of the weight of gelatin solutions containing a 0.06-mol potassium bromide, and 2000ml of water solutions containing a 7.06 mols potassium bromide and 4.4×10^{-3} mol K_2IrCl_6 for 10 minutes. pH under particle formation controlled temperature at 40 degrees C 2.0 using the nitric acid. After particle formation, the sodium-carbonate water solution was used and pH was adjusted to 6.0. Result weight was 12.53kg.

[0113] sensitization, next above-mentioned emulsion Em-1-12 -- it was alike, respectively and sensitization shown below was given. 0.5 mols of emulsion samples were fused at 40 degrees C, and sensitizing dye 1, sensitizing dye 2, and sensitizing dye 3 were added at a rate of 1:1:1 so that sum total coverage might become about 70%. Then, 4-hydroxy-6-methyl after adding TORIFOSUFINSERENAI DO, a sodium thiosulfate, chloroauric acid, and a potassium thiocyanate and

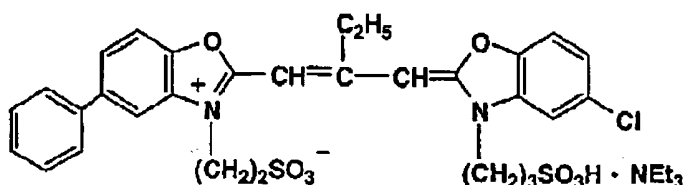
giving chemical sensitization the optimal according to a conventional method - 1, 3, 3a, a 7-tetraaza indene (TAI), and 1-phenyl-5-mercapto tetrazole (PMT) were added.

[0114] The dopant class of emulsion Em-1-12 and location where monolayer sensitized material sample production sensitization was given are shown in the following table 2. It applied to the acetic-acid cellulose film base material which covered these emulsions with the gray silver antihalation layer, respectively, and the overcoat of this emulsion layer was carried out in the 4.3 g/m² gelatin layer containing a surface active agent and a screw (vinyl sulfonyl) methane hardening agent (it is 1.75 % of the weight to gelatin AUW). Emulsion coverage (silver conversion) is 0.646 g/m², and made this layer also contain coupler 1, surface-active-agent, and gelatin total amount 1.08 g/m². Thus, samples 101-112 were produced.

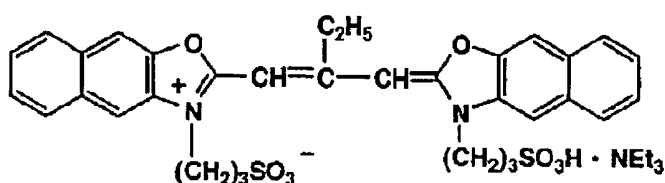
[0115]

[Formula 1]

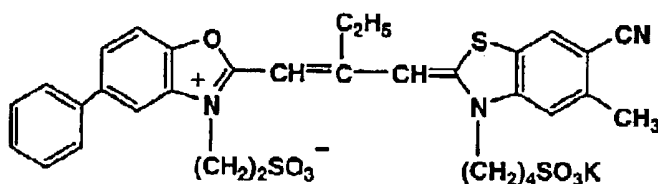
増感色素1



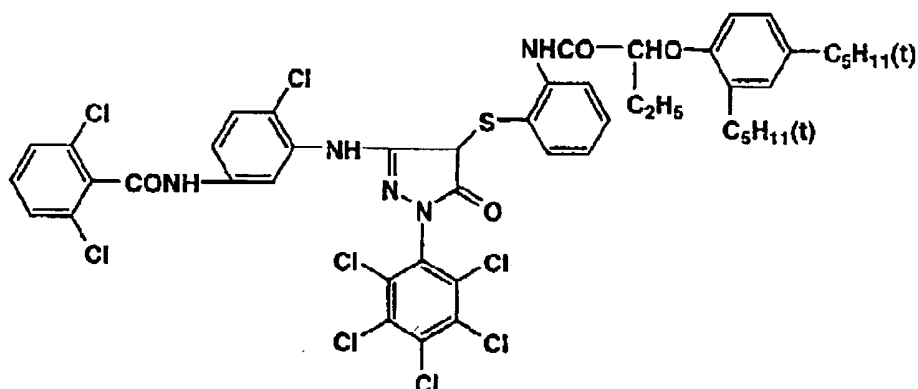
増感色素2



増感色素3



カプラー1



[0116]

[Table 2]

試料No	I r ドーパント	位置 [%]	金属ドーパント	位置 [%]	中間領域 [%]
101	—	—	—	—	—
102	K ₂ I r C l ₆	50-55	—	—	—
103	—	—	I n C l ₃	65-70	—
104	—	—	G a (N O ₃) ₃	65-70	—
105	—	—	P b (N O ₃) ₂	65-70	—
106	K ₂ I r C l ₆	60-65	I n C l ₃	65-70	無し
107	K ₂ I r C l ₆	60-65	G a (N O ₃) ₃	65-70	無し
108	K ₂ I r C l ₆	60-65	P b (N O ₃) ₂	65-70	無し
109	K ₂ I r C l ₆	55-60	I n C l ₃	65-70	5%
110	K ₂ I r C l ₆	55-60	G a (N O ₃) ₃	65-70	5%
111	K ₂ I r C l ₆	50-55	I n C l ₃	65-70	10%
112	K ₂ I r C l ₆ (微粒子)	50-55	I n C l ₃	65-70	10%

[0117] After carrying out wedge exposure respectively in 0.01 seconds and 0.0002 seconds (high illuminance) and carrying out the color development of evaluation, thus the obtained samples 101-112 according to the following down stream processing in the white light, respectively, sensibility and fogging were measured using the optical-density meter (Konica PDA-65 mold). Each relative sensibility when setting the sensibility and fogging of a sample 101 to 100 and relative fogging concentration are shown in Table 3.

[0118] Processing : Down stream processing The processing time The processing temperature color development 2 minutes and 50 seconds 38** 0.3-degree-C ** White 45 seconds It is a law 38** 2.0 degrees C. It wears. 30 seconds per minute 38** 2.0-degree-C ** Law 60 seconds 38** 5.0-degree-C ** ** 1 minute 55** 5.0-degree-C color development liquid, bleach liquor, a fixer, and slurry are as follows. It was used.

[0119]

Color development liquid Water 800 cc Potassium carbonate 30g Sodium hydrogencarbonate 2.5g Potassium sulfite 3.0g Sodium bromide 1.3g Potassium iodide 1.2mg Hydroxylamine sulfate 2.5g Sodium chloride 0.6g 4-amino-3-methyl-N-ethyl-N - (beta-hydroxyl ethyl)

Aniline sulfate 4.5g Diethylenetriamine pentaacetic acid 3.0g Potassium hydroxide 1.2g water is added, and it considers as 1l., and adjusts to pH10.06 using a potassium hydroxide or 20% sulfuric acid.

[0120]

Bleach liquor Water 700 cc 1, 3-diaminopropane tetraacetic acid iron (III) ammonium 125g

Ethylenediaminetetraacetic acid 2g Sodium nitrate 40g Ammonium bromide 150g Glacial acetic acid 40g water In addition, it considers as 1l. and adjusts to pH4.4 using aqueous ammonia or a glacial acetic acid.

[0121]

Fixer Water 800 cc Ammonium thiocyanate 120g Ammonium thiosulfate 150g Sodium sulfite 15g Ethylenediaminetetraacetic acid 2g aqueous ammonia or glacial acetic acid It uses, the water after adjustment is added to pH6.2, and it may be 1l.

[0122]

Slurry Water 900 cc PARAOKUCHIRU phenyl polyoxyethylene ether (n= 10) 2.0g Dimethylolurea 0.5g Hexamethylenetetramine 0.2g 1, 2-benzo iso thiazoline-3-ON 0.1g Siloxane (product L-77 made from UCC) 0.1g Aqueous ammonia 0.5 cc water In addition, after considering as 1l., it adjusts to pH8.5 using aqueous ammonia or 50% sulfuric acid.

[0123]

[Table 3]

試料No.	通常露光 (1" / 100)		高照度露光 (1" / 5000)		備 考
	相対感度	相対カブリ	相対感度	相対カブリ	
101	100	100	100	100	比較例
102	85	90	110	98	比較例
103	107	93	95	95	比較例
104	105	95	92	96	比較例
105	104	92	93	93	比較例
106	110	95	105	100	本発明
107	109	96	106	100	本発明
108	108	94	107	98	本発明
109	115	95	112	100	本発明
110	117	97	111	99	本発明
111	122	99	127	98	本発明
112	135	98	130	101	本発明

[0124] Even if it saw Table 3, high illuminance non-** was improved by leaps and bounds, and, moreover, as for the samples 106-112 which used the emulsion of this invention, the high sensitivity photographic emulsion which is not in the former which sensibility improved and has been formed into low fogging was able to be obtained so that clearly.

[0125]

[Effect of the Invention] High illuminance non-** was improved by leaps and bounds by this invention, and moreover, sensibility was able to improve and was able to obtain the high sensitivity photographic emulsion which is not in the former formed into low fogging.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

 CLAIMS

[Claim(s)]

[Claim 1] The silver halide emulsion characterized by containing the silver halide particle from which a silver halide particle contains combining the metallic-compounds dopant and iridium system compound dopant which are a complex centering on a kind of metal of the 7th group or the 9th group to the 14th group, or its metal ion at least from the 3rd group of the 4th, 5, and 6 period of the periodic table, and the iridium system compound dopant content section in a particle and the metallic-compounds dopant content section differ.

[Claim 2] The silver halide emulsion of claim 1 characterized by making a silver halide fine grain emulsion contain the iridium system compound dopant contained in a silver halide particle, adding, and carrying out deposition to a silver halide particle.

[Claim 3] the silver halide photosensitive material with which the silver halide emulsion of this photosensitive layer which boils further and is contained at least is characterized by being a silver halide emulsion according to claim 1 or 2 in the silver halide photosensitive material which has the photosensitive layer which contains a kind of silver halide particle at least on a base material.

[Translation done.]